MEASUREMENT OF O_2 CONCENTRATION BEHIND SHOCK WAVES USING AN ULTRAVIOLET ABSORPTION TECHNIQUE

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In connection with studies of the effect of dissociation on gas properties and of the relaxation time for dissociation under various flight conditions, a method has been developed by the Langley Research Center for measuring the concentration of molecular oxygen as a function of time behind shock waves. The technique is based on the ability of the oxygen molecule to absorb ultraviolet light in the wavelength range 1,250 to 1,750 angstrom units, whereas atomic oxygen is transparent to these wavelengths. Work very similar to this has also been reported by the Avco Research Laboratory.

The main objectives of this paper are to describe the method and the equipment. It starts with a brief discussion of what is meant by absorption and in particular what sort of absorption occurs in oxygen - that is, how strong is the absorption of light in oxygen and how does the absorption coefficient vary with temperature and wavelength. A description of the shock tube and the instrumentation follows. Also a typical record is shown and is correlated with theoretical curves which show how light absorption should vary in the shock tube for various reasonable assumptions about the state of the gas behind a shock wave.

For the benefit of anyone who would like to be reminded of just what is meant by the term "absorption" figure 1 shows the equation for absorption of monochromatic light in passing through a given thickness of

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gas. I/I_o is the fraction of light which passes through the gas layer without being absorbed. The absorption coefficient k varies with temperature and the wavelength of light. Since it is defined in terms of gas at standard temperature and pressure an equivalent path length l' is used in the equation instead of the actual path length l. This equivalent path length is obtained by converting test conditions to standard conditions.

Figure 2 shows the absorption coefficient of molecular oxygen as a function of wavelength and temperature in the region of interest. It is the continuous absorption associated with the Schumann-Runge band system of oxygen and lies in the vacuum ultraviolet part of the spectrum - which, incidentally, is so named because spectrographs have to be highly evacuated to prevent complete absorption of all light by the oxygen present in the air. These absorption coefficient curves are calculated results obtained at the Langley Research Center. They are adjusted so as to match experimentally observed values which have been reported in the literature. Since all the literature data were taken at room temperature it will be interesting to check the high temperature curves experimentally with the shock-tube results. This can be done if conditions behind the shock front are known independently. For instance, if the shock Mach number is not too high little or no dissociation is present immediately behind the shock front and the other degrees of freedom, such as translation, vibration, and rotation, are in equilibrium.[1]

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[1]Avco's studies show that, while this statement is true for oxygen, it is not true in air. The time required for vibrational equilibrium in nitrogen is of the same order of magnitude as the dissociation time of O_2. (Avco Research Report 22.)

Thus temperature, density, and gas composition are known - leaving only the absorption coefficient to be determined from measurement of the change in transmitted light. Preliminary examination of the data in hand from this point of view has thus far proved satisfactory. Investigation of the temperature dependence of the absorption coefficient by this means will be continued.

Figure 3 shows a block diagram of the experimental setup used. Ultraviolet light from a pulsed hydrogen discharge tube passes through a 1-inch absorption path and a grating monochromator before it falls on a photomultiplier sensitized for ultraviolet light with sodium salicylate. Because of the oxygen present in air all light paths are in vacuum. The bandpass width of the monochromator is about 11 angstroms. A Polaroid Land camera is used to photograph the trace on a Tektronix 545 oscilloscope. The time resolution of the system is determined by the time required for the shock wave to cross the light beam and is approximately one-third of a microsecond. Ionization probes located 5 inches in front of and 5 inches behind the test section are used for the shock velocity measurements and to trigger the light source and scope sweep.

Two of the many discharge tube configurations which have been tried are shown in figure 4. Since development work on the light source is still being carried on a general discussion of features common to all types tried will be given. The discharge takes place in flowing hydrogen at about 1 to 2 mm pressure. There is no window between the discharge and the lithium fluoride shock-tube window. Care is taken to insure

the cleanliness of the glass and metal surfaces exposed to the discharge, but no elaborate outgassing procedures are used. The current pulse is of the order of 2,000 amperes and is obtained from an artificial transmission line made up of 20 condensers and 20 coils. The use of an artificial transmission line for energy storage gives the light pulse a long duration and a flat top. A heavy duty hydrogen thyratron is used to hold off the discharge until a triggering pulse is received from the shock tube.

The shock tube used (see fig. 5) has been described in the Journal Aeronautical Sciences (August 1958 issue) by Schexnayder. It is a double diaphragm type with a 16 to 1 area contraction just before the second diaphragm. The buffer chamber is filled with helium and the high pressure chamber is filled with helium or hydrogen-helium mixtures, depending on the Mach number desired. The high-pressure diaphragms are 1/16-inch scribed steel plates. The low-pressure diaphragms are Mylar film. The high-pressure diaphragm is broken by pressure. The low-pressure diaphragm is broken by the reflection of the primary shock wave at the contraction. The pressure in the 1-inch-diameter portion of the shock tube is always determined by the partial pressure of O_2 necessary to give a convenient amount of ultraviolet light absorption. For pure O_2 this pressure is about 0.3 mm and for a 10 percent O_2 in argon mixture is about 3 mm. The low-pressure section is always pumped to 20 microns before filling and is raised to the desired initial pressure by admitting the gas mixture through a leak valve while continuing the pumping. Thus the runs are

taken in a slowly flowing mixture. The effects of residual vapor pressures and small air leaks are minimized by this procedure. The leak rate of the shock tube when closed off from the pump is 1 or 2 microns per minute.

Figure 6 illustrates a typical record obtained from a shock-tube run. The shape of the ultraviolet light pulse used as background for absorption is indicated by the dotted line. The sudden decrease in light intensity as the shock enters the absorption beam indicates that the amount of molecular oxygen in the path has increased. This is because of the increase in gas density across the shock front. The further decrease in light intensity shows that the amount of molecular oxygen increases still more as the dissociation proceeds. The useful part of the record is terminated by the arrival of the driver gas. It may seem paradoxical that the amount of molecular oxygen in the path should increase as a result of the dissociation of molecules into atoms. To make clear what happens look at the equation for absorption, which can be written like this:

$$\frac{I}{I_o} = e^{-\text{Constant}\left(\frac{1-\alpha}{1+\alpha}\right)k_T \frac{\rho}{\rho_1}}$$

I/I_o is the fraction of light which gets through the shock tube without being absorbed. The degree of dissociation is indicated by α. The absorption coefficient is not a function of wavelength during a run because the monochromator is set at a fixed wavelength, but it is written in the equation as k_T to indicate its temperature dependence. The

density ratio across the shock wave is ρ/ρ_1. Immediately behind the shock wave $\alpha = 0$ and $\frac{1+\alpha}{1+\alpha} = 1$. The density increase has a larger effect than the change in the value of k_T. Thus, as has already been stated, the increase in absorption noted when the shock front passes is primarily due to the density increase. In the relaxation zone behind the shock front the degree of dissociation is not zero but increases with distance from the shock front. The temperature falls as the dissociating molecules take up thermal energy, and the density ratio ρ/ρ_1 becomes larger. Under the conditions present for the record illustrated the density increase overpowers the other factors and causes increased light absorption even though the gas is dissociating. Note, however, that the density increase is not always predominant. Records are often obtained which show decreasing absorption as dissociation proceeds. Behind very strong shock waves the temperature is high enough to produce complete dissociation. In this case $\alpha \to 1$, $\frac{1+\alpha}{1+\alpha} \to 0$, and $\frac{I}{I_o} \to e^0 = 1$. Thus, there is no absorption of light at all when the oxygen molecules are all dissociated.

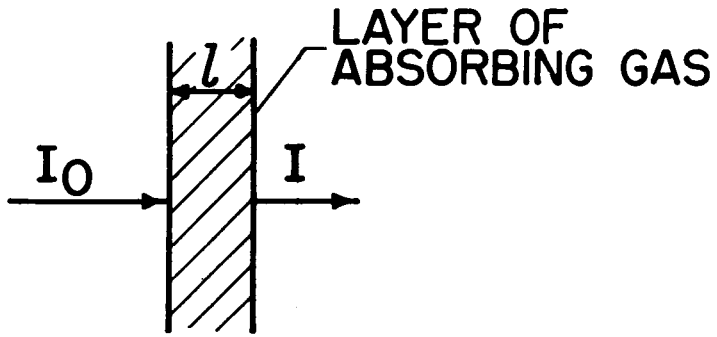
Some of these considerations are illustrated in figure 7, which shows percent transmission of light as a function of Mach number for various assumptions about the state of the gas. The horizontal line at the top marked "Initial" represents the amount of light being transmitted before the shock wave passes. The curve marked "Constant γ" at the bottom

represents the amount of light transmitted after the shock passes if it is assumed that vibration and dissociation are both frozen. The "Frozen Dissociation" curve represents the amount of light transmitted if only the dissociation is frozen, while vibration is assumed to be in equilibrium. The curve marked "Equilibrium" represents the amount of light transmitted when both dissociation and vibration are in equilibrium. For a given shock wave the percent transmission at first lies on the "Initial" curve, drops to the "Frozen Dissociation" curve immediately behind the shock front and adjusts to the "Equilibrium" curve in the relaxation region. Note that this final adjustment may be in either direction - depending on the relative position of the two curves at the Mach number in question. Also note that for high Mach number the "Equilibrium" curve goes to 100 percent transmission - indicating complete dissociation of the oxygen.

Figure 8 shows a plot like the one in figure 7, but this time it is for a particular gas - namely pure oxygen at an initial pressure of 0.3 mm. The notation is the same as before. Experimental points are plotted on this figure for the gas in front of the shock, immediately behind the shock and at the end of the available testing time. These points agree fairly well with the theoretical curves, but better agreement is hoped for as the technique and equipment improve. The theoretical curves depend on calculated values of the absorption coefficient and may need revision if better values of the absorption coefficient are found.

It is evident that the relaxation time for dissociation of oxygen under conditions actually present in the shock tube can be read directly from the records. The reaction rate for dissociation can also be evaluated from the records, but a rather careful analysis is necessary. The records we have are being analyzed to obtain the reaction rate. To date the results are preliminary and a bit rough. However, they are in substantial agreement with those published by Avco.

Summarizing quickly, an ultraviolet absorption technique has been tested and found suitable for studies of processes which involve rapid changes in the concentration of molecular oxygen. In particular, it has been applied to the study of the dissociation of molecular oxygen into atomic oxygen behind a shock wave. The time resolution is good - being about one-third of a microsecond for the equipment described.



$$\frac{I}{I_0} = e^{-kl'}$$

I_0 = INTENSITY OF LIGHT ENTERING ABSORBING LAYER

I = INTENSITY OF LIGHT EMERGING FROM ABSORBING LAYER

k = ABSORPTION COEFFICIENT

l = ACTUAL PATH LENGTH

l' = EQUIVALENT PATH LENGTH AT STANDARD SEA LEVEL DENSITY

Figure 1.- Light absorption in gas layer. NASA

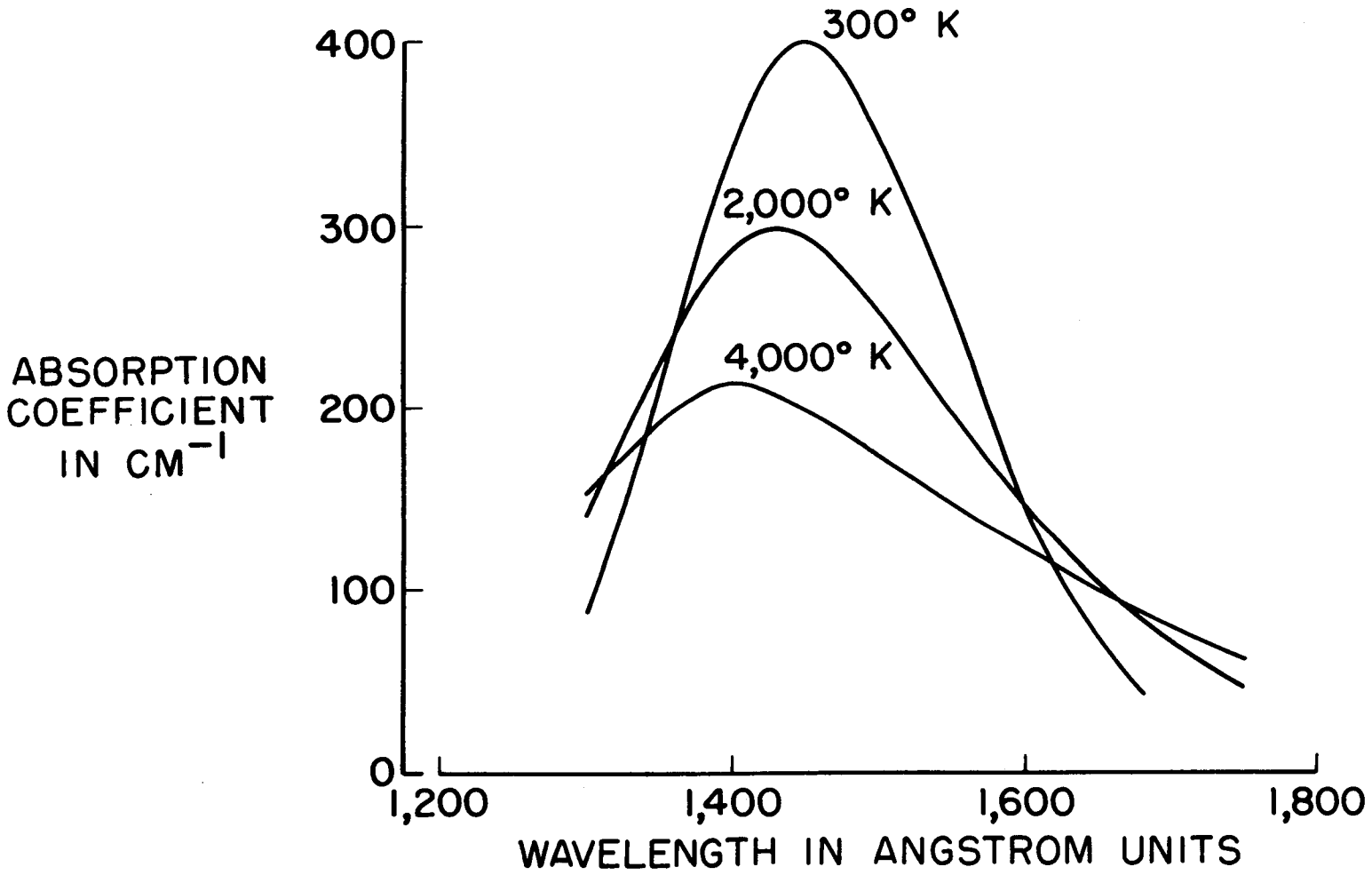


Figure 2.- Absorption coefficient of molecular oxygen as a function of wavelength and temperature. NASA

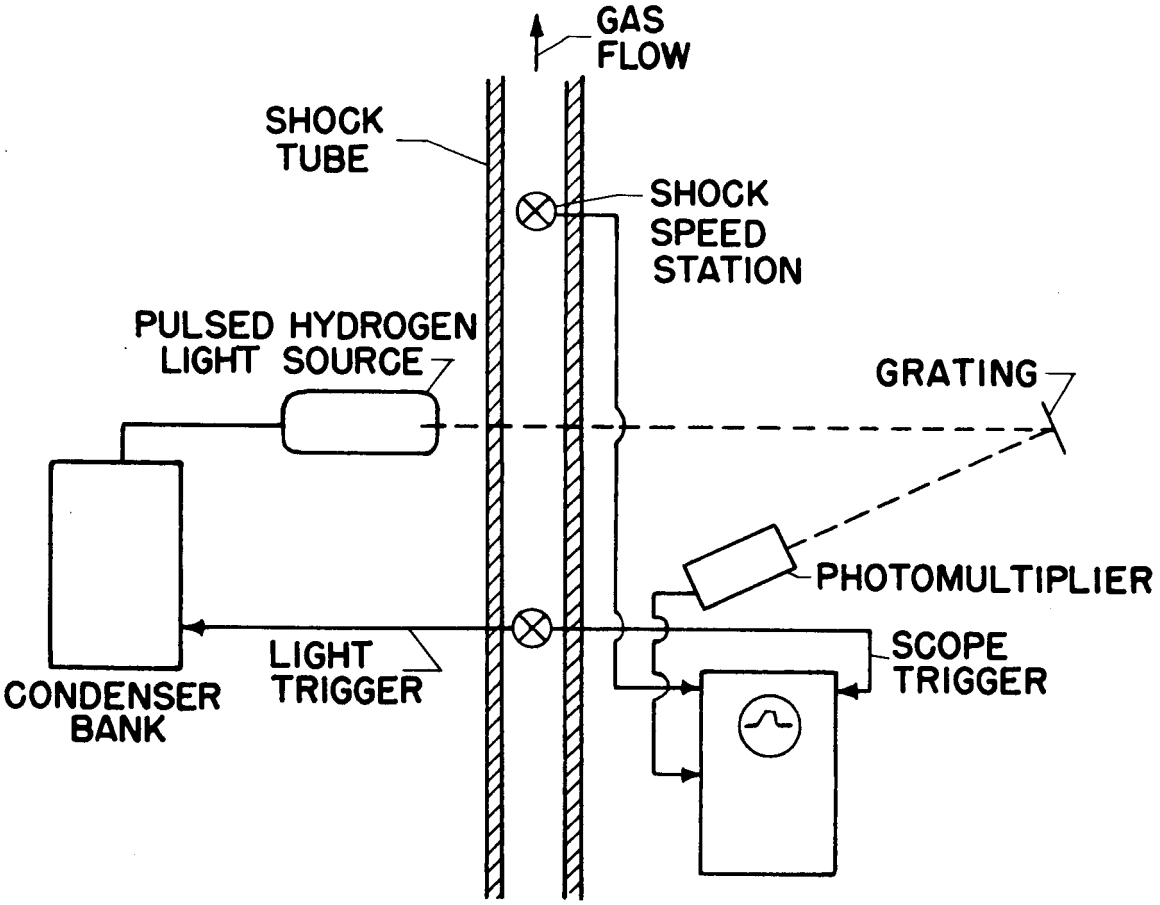


Figure 3.- Schematic diagram of equipment. NASA

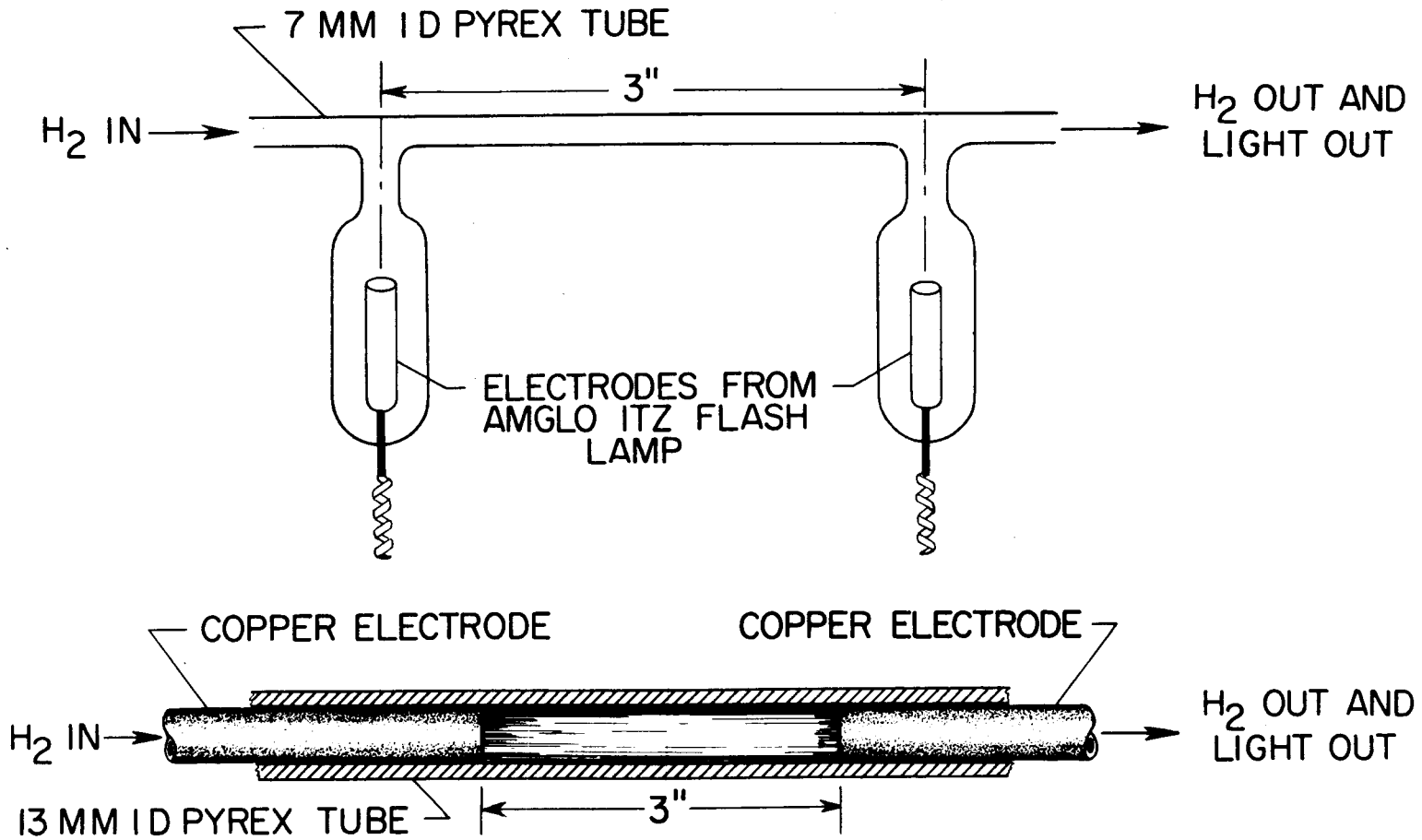


Figure 4.- Two hydrogen discharge tube configurations. NASA

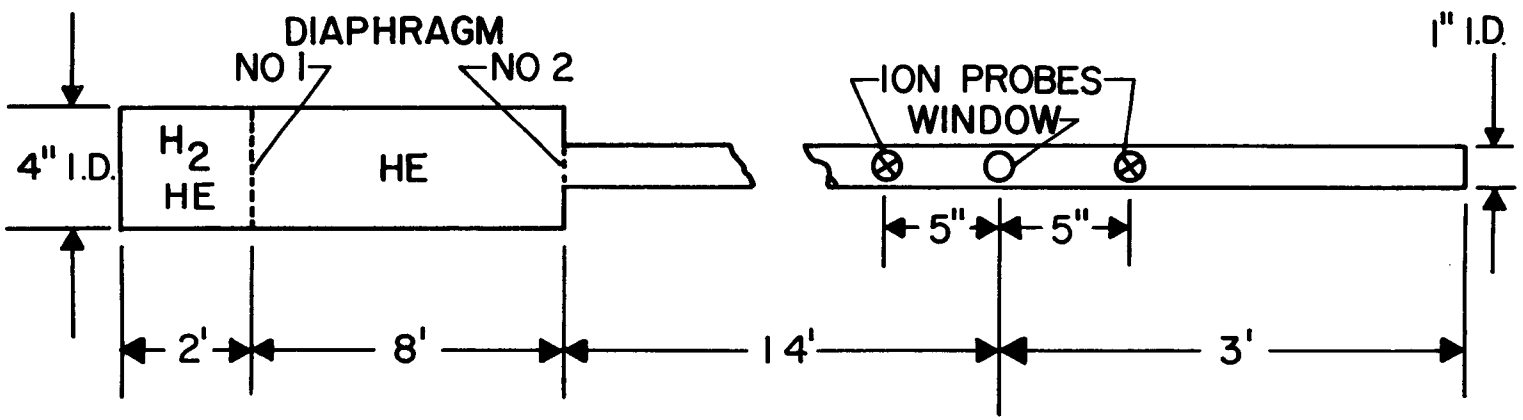


Figure 5.- Double diaphragm shock tube. NASA

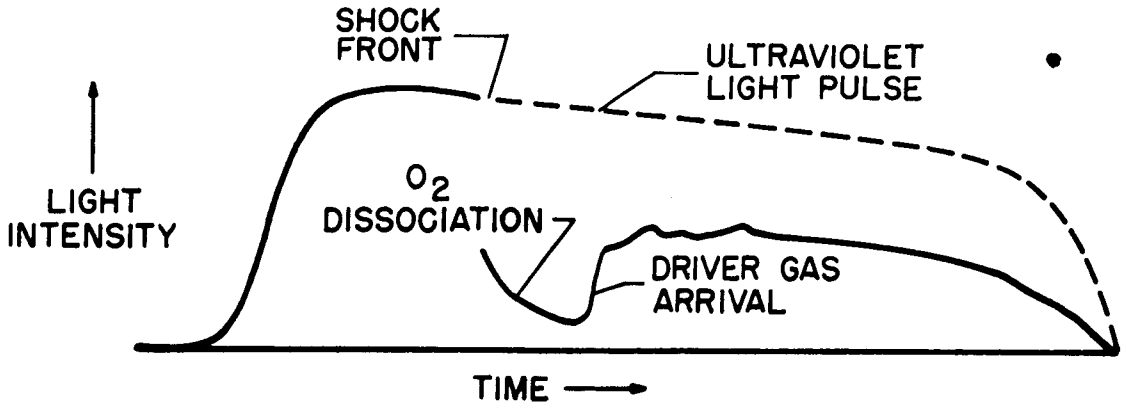


Figure 6.- Oscillogram showing ultraviolet absorption. NASA

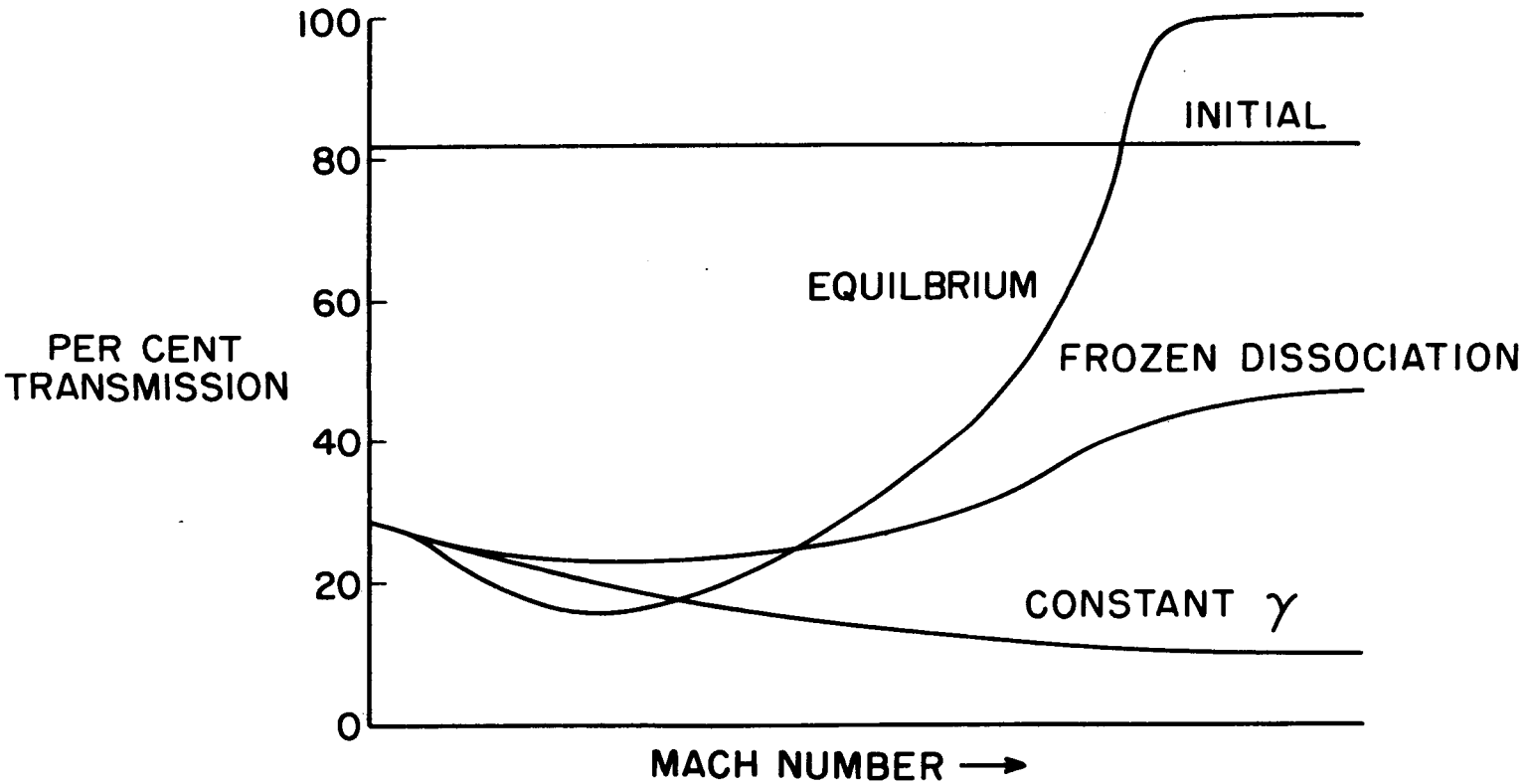


Figure 7.- Percent transmission of ultraviolet light through absorbing gas layer. NASA

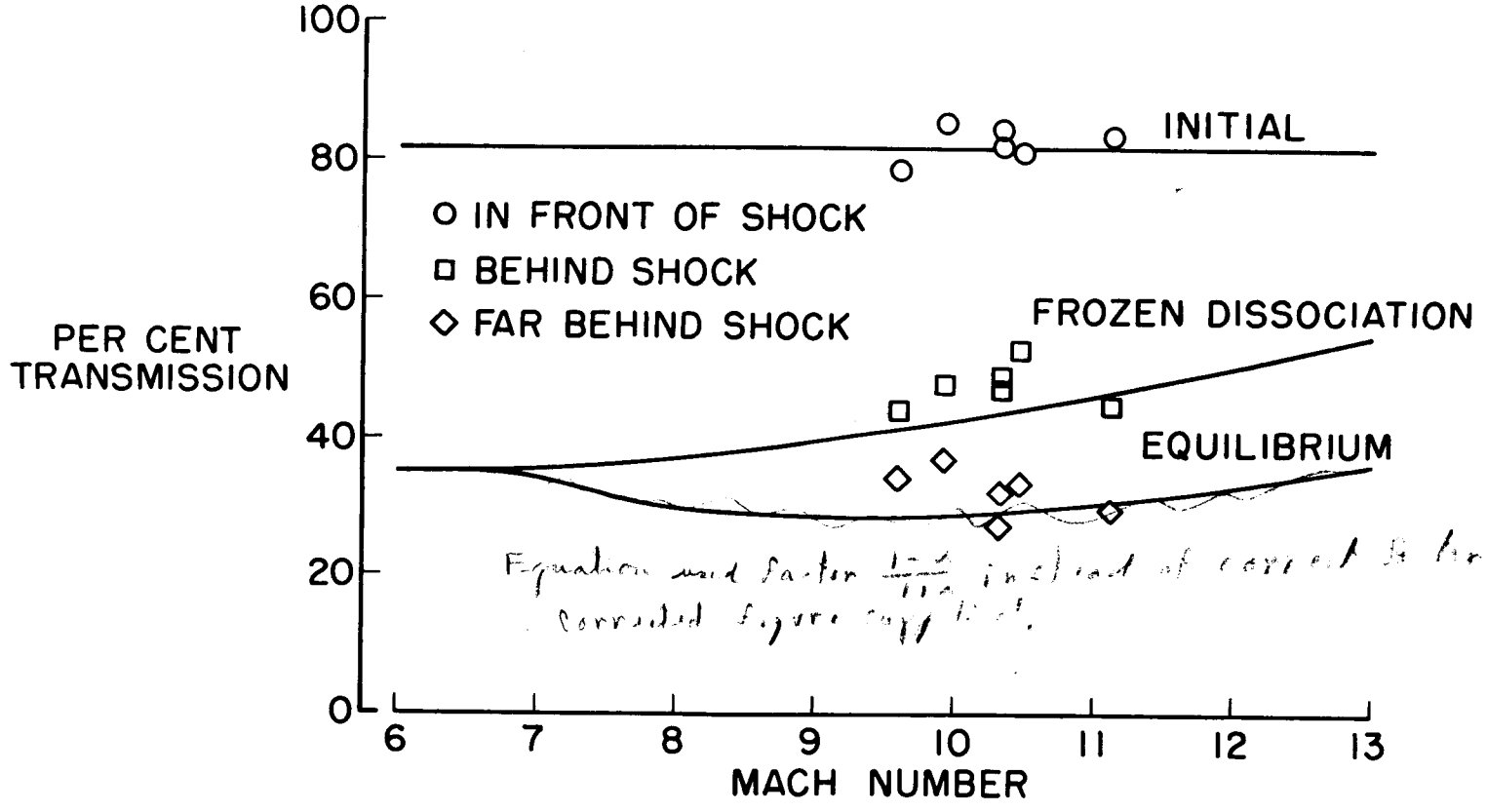
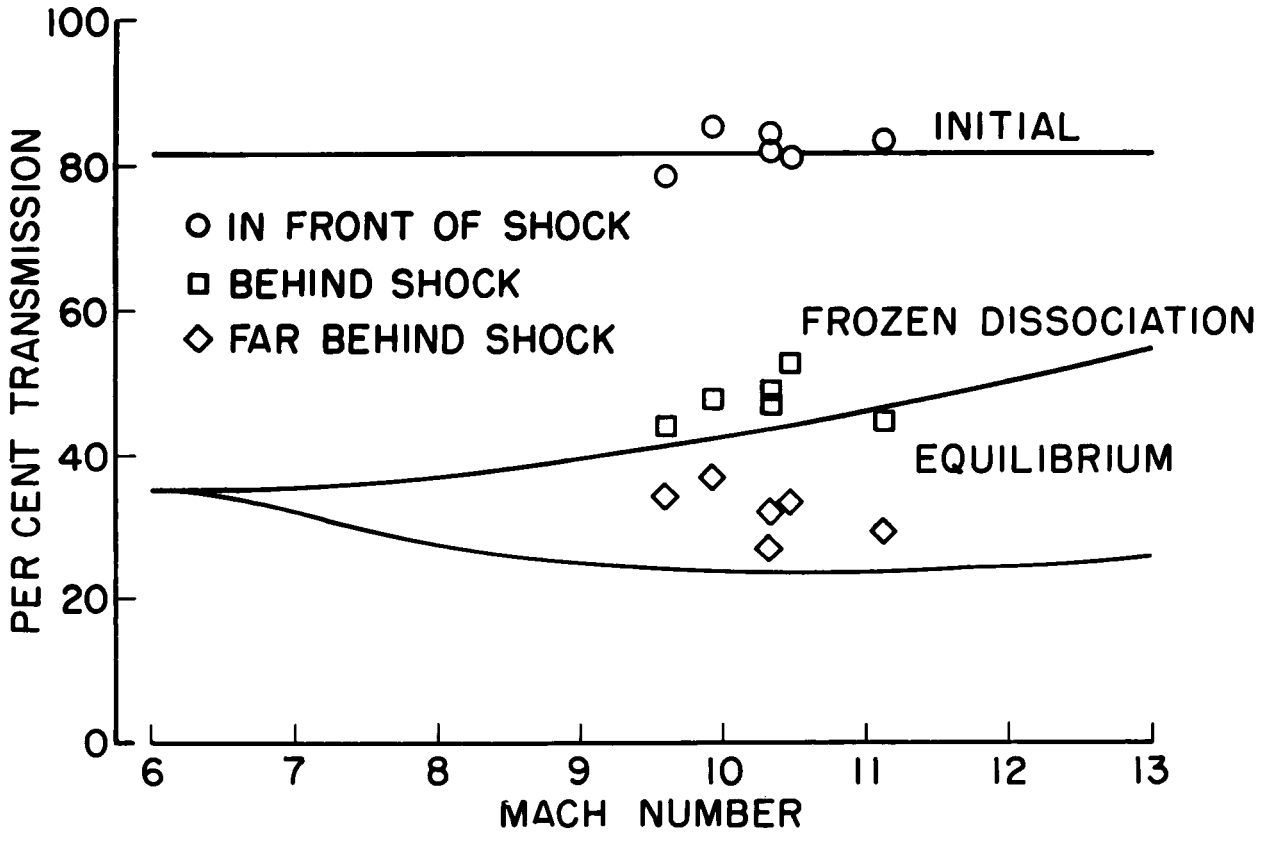


Figure 8.- Percent transmission of ultraviolet light through test section containing pure oxygen at 0.3 mm Hg.

NASA



NASA

Figure 8.- Percent transmission of ultraviolet light through test section containing pure oxygen at 0.3 mm Hg.